

# METHOD FOR GASIFYING ORGANIC SUBSTANCES AND SUBSTANCE MIXTURES

## AND APPARATUS

The invention relates to a method for gasifying organic substances and substance mixtures ~~according to the generic terms of Claim 1.~~

From US-PS 4,568,362, a method for gasifying organic substances and substance mixtures is known in which the organic substances are directed into a pyrolysis reactor in which the organic substances come into contact with a heat carrier medium which causes rapid pyrolysis in which the organic substances are converted into pyrolysis products, that is, pyrolysis gases with substances that can be condensed and solid residue containing carbon. The heat energy needed for the pyrolysis is generated by firing the solid residue containing carbon. In a second reaction zone, the pyrolysis gases that contain tar are subjected to cracking reactions and reactions with steam such that a product gas with a high caloric value is obtained.

In this method, the pyrolysis as well as the firing of the solid residue containing carbon take place in a fluidized bed. In the upper part of the pyrolysis fluidized bed reactor, a reaction zone is provided for the pyrolysis gases containing tar.

The heat carrier medium is discharged together with the solid residue containing carbon in part through the reactor head of the pyrolysis fluidized

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A<sub>2</sub>A<sub>2</sub> BACKGROUND OF THE INVENTION

bed reactor and the remaining portion via a line that is mounted on the upper fluidized bed limit, and fed to the fluidized bed firing. There, the solid residue containing carbon is fired and the heat carrier medium heated up. The heated heat carrier medium and the ashes are discharged from the fluidized bed firing together with the waste gas, and separated in a gas-solid separator mounted above the fluidized bed pyrolysis reactor, and fed to the reaction zone of the pyrolysis reactor from which it again falls into the fluidized bed of the pyrolysis reactor (heat carrier medium cycle).

It is very costly to operate the fluidized beds and it is hardly possible to control the reactions of the pyrolysis gases in the reaction zone.

*INS A<sub>3</sub> >* ~~The object of the invention is to make available a method for generating a gas with a high caloric value that is easy to perform. In this process, a small condensation portion is preferred. A further object of the invention is to make available a simple apparatus for carrying out the method.~~ *AND AN APPARATUS PERFORM AND RESULTS IN*

*INS A<sub>4</sub> >* ~~With respect to the method, this object is resolved by the combination of features in Claim 1.~~ *SUMMARY OF THE INVENTION*

According to the invention, the pyrolysis is carried out in a fluidized bed reactor or a rotary drum, the pyrolysis gases are mixed, if necessary, with a reactant such as steam, and they are fed into an indirect heat exchanger in which the pyrolysis gases react with the reactant. The solid residue containing carbon and the heat exchanger medium are fed to a firing. The firing waste gases are fed through the indirect heat exchanger such that their heat content is used for the reaction of the pyrolysis gases with the reactant. The ashes of the solid residue containing carbon and the heat carrier medium taken from the firing are fed into the pyrolysis reactor at the entry end for the organic substance.

The invention involves the basic concept that gasifying methods should be divided into three method steps that can be carried out easily. In a first method step, pyrolysis of the substances used takes place rapidly. In the process, the goal is to have as little as possible of the condensable substances in the pyrolysis gases. The rapid pyrolysis is ensured by performing the pyrolysis of the substances used at a temperature of 550-650°C.

In a second method step, the pyrolysis gases are heated and reacted with steam to adjust the product gas quality. The reaction of the pyrolysis gases is carried out with steam at a temperature of 900-1000°C.

In a third method step, the solid pyrolysis residue containing carbon is fired. The heat generated in the process is used for the pyrolysis and the reaction of the pyrolysis gases. Furthermore, the heat carrier medium is heated up in the firing and then is conveyed back into the pyrolysis reactor. The heat transfer for the reaction of the pyrolysis gases with steam takes place in a heat exchanger that is heated by the waste gases from the firing.

The advantage of this division of the three method steps is that each method step and the combination of the method steps can be arranged according to the set standard of gas product quality.

The set standard for the gas product quality is first of all, a higher caloric value. Furthermore, the steam content is increased by the second method step so that the gas product is very well suited for use as a synthesis gas, and energy use in connection with fuel cells can also be considered. Naturally, use to obtain energy via a gas motor or gas turbine is also possible.

The reactant is steam. It is possible to avoid the addition of steam when sufficient water vapor is contained in the feedstock used, for example, when the material used is not dried or only to a limited extent. Furthermore, it is possible that the pyrolysis gases that form contain sufficient water vapor when sufficient steam develops in the pyrolysis of the substances used. It is also possible to provide the addition of steam in the pyrolysis step.

With the method according to the invention, basically all organic substances and substance mixtures can be gasified. However, it is preferable to gasify biomasses.

The substances used must be pretreated before they are fed to the pyrolysis. The pretreatment is generally limited to drying and if necessary, to pulverization. In the process, no great restrictions are set for the lumpiness of the substances used because the pyrolysis is carried out in a fluidized bed with a heat carrier medium.

To improve the cracking of the noncondensable substances in the pyrolysis gas, a catalyst can be provided in the reaction of the pyrolysis gases with steam. Preferred catalysts are dolomite, calcite, nickel, nickel oxide, nickel aluminate, or nickel spinel.

5        When dolomite is used, it is advantageous to calcinate the dolomite at the reaction temperature of 900-1000°C, and the resulting calcium/magnesium oxide has particularly high catalytic activity.

10        The reaction temperature of 900-1000°C is advantageous for the reaction of the pyrolysis gas with steam, because in this temperature range, the sulfur sensitivity of the named catalysts is very much reduced. There is the possibility of regenerating the catalysts from time to time in situ by the addition of a small amount of air at temperatures above 1000°C.

15        The catalysts can also be used as a heat carrier medium. This manner of proceeding has the advantage that the catalysts are periodically regenerated in the heat carrier cycle.

To prevent the catalyst from being deactivated by dust, it is recommended that the hot pyrolysis gases be dedusted before addition of the steam.

20        In cases in which, because of the substances used, there is only minimal development of pyrolysis coke and thus the heat developing in the firing is not sufficient for pyrolysis and reaction with steam, a portion of the pyrolysis gas can be fired to generate heat.

25        The firing of a portion of the pyrolysis gas to generate heat is also required when the pyrolysis coke is used as a material, for example, for the production of activated charcoal or grilling charcoal or charcoal briquettes. So that the pyrolysis coke can be transferred out well, the grain size of the heat carrier medium must be small enough that the heat carrier medium can be separated from the pyrolysis coke without any problem.

30        For the device according to the invention, simple and cost-effective components can be used that are known as such and easily available. With these components, the device according to the invention can easily be constructed.

The pyrolysis takes place in a moving bed reactor using a heat carrier medium. A shaft kiln is primarily used for this into which the mixture consisting of the material to be gasified and the heat carrier medium is loaded from above. The mixture travels through the shaft kiln. Rapid pyrolysis occurs due to the intimate contact of the material used with the heat carrier medium.

So that even with heterogeneous materials, transport through the shaft kiln is ensured, built-in structures or spiral conveyors can be provided inside the shaft kiln. The built-in structures also have the advantage that the pyrolysis gases developing can better escape upwards through the moving bed. Nevertheless, the equipment expense is increased in this way.

Basically, the pyrolysis can also be carried out in a rotary drum or a double-deck oven, although here as well, the equipment cost would be greater.

The mixture consisting of the heat carrier medium and the pyrolysis residue can be transferred into the firing via commercially available aggregates such as conveyor worms, swivel grates, rotating grates or cellular wheel sluices. In combination with a grate firing, however, the use of feeding rams is preferred. When an underfeed stoker is used, the use of conveyor worms is preferred. The firing waste gases are fed through an indirect heat exchanger that simultaneously serves as chemical reactor in which the pyrolysis gases react with steam. Such heat exchangers are known, for example, in refineries as steam reformers or reformers.

Also for the conveyance of the heat carrier medium from the firing into the shaft kiln, conventional conveyance devices can be used, such as vibrating conveyors, bucket conveyors, or chain conveyors. The demands on conveyance technique also correspond to the requirements that appear in the steel industry or in the field of coking, so that excessive expense is not required for layout of the aggregates.

The heat carrier medium must have sufficient mechanical, chemical, and thermal stability in the temperature range of 600-1000°C. Fire-resistant substances such as sand, silicon, grit, aluminum silicates, corundum, graywacke, quartzite, or cordierite are used. The use of molded bodies of metallic or non-

metallic materials or combinations of them, such as steel or ceramic balls is also possible.

5 With respect to the particle size, the heat carrier medium must be fine enough to be able to make intimate contact with the material used so that a good transfer of heat can take place. On the other hand, the particles of the heat carrier medium must be big enough that there is sufficient empty volume through which the pyrolysis gases can flow.

10 These requirements are best fulfilled when the heat carrier medium has a grain size of 1-40 mm. This grain size also has the advantage that the heat carrier medium can be separated well from the ash of the pyrolysis residue after the firing.

15 As mentioned above, a catalyst can be provided for the reaction of the pyrolysis gases with steam. For this purpose, a catalyst bed can be mounted in the heat exchanger. Depending on whether the pyrolysis gases are fed through the pipes of the heat exchanger or outside the pipes through heat exchanger, the catalyst bed is mounted inside or outside of the pipes of the heat exchanger. It is also possible to use a catalytically active material for the heat exchanger pipes such as corundum with nickel or nickel oxide. It is also possible to provide a solid bed reactor with a catalyst bed behind the heat exchanger.

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If the reaction of the pyrolysis gases with steam is to be supported by a catalyst, it is recommended that the hot pyrolysis gases be dedusted with a filter before contact with the catalyst.

25 The method steps named above as well as those claimed and described in the embodiment example, which are to be used according to the invention, as well as structural components are not subject to any special exceptional restrictions with respect to their method restrictions, their size, shape, material selection, and technical conception, so that the selection criteria known in the particular area of application in each case can be used without any limitations.

30 <sup>125</sup>A 5 ~~Further details, features, and advantages of the object of the invention result from the following description of the related illustration in which, as an~~

~~example, a preferred embodiment of the gasifying of organic materials is represented. Shown in the illustration are:~~

Figure 1, a diagram of the method according to the invention,

Figure 2, the mass and energy balance of the pyrolysis and reaction

5 steps,

Figure 3, the mass and energy balance of the firing, and

Figure 4, a schematic representation of a device for carrying out the

method according to the invention.

method according to the invention.

5 ~~It is evident from Figure 1 that the material to be gasified 1 is fed into~~

*DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS*

pretreatment step 2. Depending on the material, this can be a drying and/or pulverization device in which the material is prepared for the subsequent pyrolysis. The pretreated material 1 is brought into pyrolysis step 3. The pyrolysis step 3 leaves a pyrolysis gas 5 and a pyrolysis coke 5a.

The pyrolysis coke 5a is fired in firing 6. The heat from firing 6 is directed via a heat coupling 7 to pyrolysis step 3 and via a heat coupling 7a to a reaction zone 4 for pyrolysis gas. The waste gases 18 of firing 6 are cooled and diverted in a flue gas cleaning and cooling step 17. The waste heat obtained with the flue gas cleaning and cooling step 17 can be used, for example, for the drying in pretreatment step 2.

Depending on the method conditions, more heat may develop in firing 6 than is needed for heat coupling 7 and 7a. Steam can be generated with this heat. For this, feed water 9 can be fed via water treatment 10 and pump 11 into heat exchanger 12 which is mounted in firing 6. The steam 16 generated is fed into reaction zone 4. The pressure of the unneeded portion can be released via turbine 13 and further utilized as waste steam 16a.

The pyrolysis gas 5 is fed into reaction zone 4 with steam 16. In this reaction zone, the pyrolysis gas and the crack products of the condensable substances are reacted with steam to the desired gas product 15. The gas product 15 is then purified in a dedusting 8 and fine dedusting and quenching 14. It is also possible to feed a portion 19 of the gas product 15 into pyrolysis 3.

The addition of air and/or oxygen can be provided in the individual

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off heat. In this way, heat carrier medium 414 is heated to approximately 1000°C. Heat carrier medium 414 consists of a coarse grained material such as sand, gravel, or split. During the firing, heat carrier medium 414 and pyrolysis coke 426 travel as far as worm 408 at the end of grate 405, by which the ash of pyrolysis coke 426 and heat carrier medium 414 are discharged. The majority of this mixture consisting of heat carrier medium 414 and ash is returned to shaft kiln 403 via conveyance 409 and sluice 410, where heat carrier medium 414 discharges the heat absorbed in firing 407 to material 401.

A small portion of the mixture consisting of ash of pyrolysis coke 426 and heat carrier medium 414 is discharged via cooling 411 and sieve 412. Through sieve 412, the ash of pyrolysis coke 426 is separated as fine material 413 from the coarser heat carrier medium 414 and heat carrier medium 414 is returned to the process. This separation is superfluous when the material to be gasified does not contain any ash-forming constituents.

The pyrolysis gas forming during the pyrolysis in shaft kiln 403 is withdrawn from the upper area of shaft kiln 403 via line 403a and fed into heat exchanger 417. Aside from water, carbon monoxide, carbon dioxide, hydrogen, and methane, the pyrolysis gas also contains higher hydrocarbons and tars as well as other organic, especially aromatic compounds as condensable components. Heat exchanger 417 is heated to a temperature of approximately 950°C by the waste gases of firing 407. At this temperature, the pyrolysis gas and the condensable substances react with steam that is contained in the pyrolysis gas. In addition, ~~steam 416~~ is fed into line 403a for the reactions in heat exchanger 417. To further increase the temperature in heat exchanger 417, air 415 can also be added for a partial firing of the pyrolysis gas. To improve the cracking of the accompanying tars, a catalyst can be provided in the heat exchanger.

It is also possible to add the catalyst in the flow stream to the pyrolysis gas stream and to separate it again after heat exchanger 417 and reuse it.

Heat exchanger 417 leaves a gas product whose portions of carbon monoxide and hydrogen have been maximized. This gas is fed to heat ex-

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changer 421 for utilization of waste heat and into washer 422 for gas purification.

Gas product 425 is withdrawn via induced draught ventilator 423.

5 The waste heat from heat exchanger 421 can be used to heat the pyrolysis gas to reaction temperature for the reaction with steam.

After it has flowed through heat exchanger 417, the waste gas of firing 407 is fed through heat exchanger 418 for waste heat utilization. After gas purification 419, waste gas 424 is discharged to the surroundings via induced draught ventilator 420.

10 Both firing 407 and also heat exchanger 417 are operated at a pressure that only slightly deviates from atmospheric pressure and generally is somewhat less than the latter. Induced draught ventilator 423 for gas product 425 and 420 for waste gas 424 are regulated and coordinated with one another so that the pyrolysis gas is fed through heat exchanger 417 and is not sucked through the shaft oven feed into firing 407.

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~~Embodiment example~~

### EXAMPLE 1

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1000 kg/h wood are gasified in the device according to Figure 4. The wood contains 3% ash (free from water) and otherwise consists essentially of 50% carbon, 6% hydrogen, 42% oxygen, and 1.9% nitrogen, calculated without water or ash. The upper caloric value is 17.9 MJ/kg in the anhydrous state. The thermal gasification efficiency is 4.97 MW. The pyrolysis is carried out at 600°C and the reaction with steam at 950°C. The working pressure is atmospheric pressure.

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Gravel with a grain size from 3 mm to 15 mm is used as heat carrier medium. The gravel is heated from 600°C to 950°C. Because of the required thermal performance of 380 kW, the cycling quantity of the heat carrier medium is five times that of the wood input, that is, 5000 kg per hour. The shaft kiln is 4.5 m high and has a diameter of 1.5 m, corresponding to a fluidized bed volume of 7.5 m<sup>3</sup>. The residence time in the shaft kiln is two hours.

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In the pyrolysis, the wood is reacted so that 20 wt% of the wood remains

as wood charcoal. In the following table, the quantities and compositions of the wood and pyrolysis coke (wood charcoal) are listed:

Material flow	Wood	Wood charcoal
m [kg/h]	1000	200
H <sub>u</sub> [MJ/kg] dry	17,9	33,5
C [wt%] daf	52,1	92,2
H [wt%] daf	4,8	2,6
O [wt%] daf	42,4	5,2
Ash [wt%] dry	3,4	17,0

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The following gas product is obtained:

Caloric value [MJ/Nm <sup>3</sup> ]	10,5
H <sub>2</sub> [Vol.-% dry]	51,1
CO [Vol.-% dry]	39,7
CH <sub>4</sub> [Vol.-% dry]	0,01
CO <sub>2</sub> [Vol.-% dry]	9,2
H <sub>2</sub> O [Vol.-%]	14,8
Chemical. enthalpy flow [MW]	3,9
Quantity [Nm <sup>3</sup> /h]	1.338

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The enthalpy flow of the wood charcoal in the firing is 1.86 MW. This is sufficient to generate a steam flow of 0.45 MW (360 kg/h at 950°C and atmospheric pressure) as well as to cover the heat requirement of the reaction of the pyrolysis gas with steam at the level of 0.84 MW. The firing efficiency is 85%.

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After accounting for the heat loss and loss through the waste gas flow, only

0.26 MW remain. With this, 324 kg/h superheated steam were generated that were relaxed via a turbine and used as heating steam. The cold gas efficiency is 79%.

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## List of reference numbers:

- 5 1 Material used  
2 Pretreatment step  
3 Pyrolysis  
4 Reaction zone  
5 Pyrolysis gas  
5a Pyrolysis coke  
6 Firing  
10 7 Heat coupling  
7a Heat coupling  
8 Dedusting  
9 Feed water  
10 Water treatment  
15 11 Pump  
12 Heat exchanger  
13 Turbine  
14 Fine dedusting/quenching  
15 Gas product  
20 16 Steam  
16a Waste steam  
17 Heat exchanger/flue gas cleaning  
18 Waste gas  
19 Gas product  
25 20 Air  
101 Pyrolysis step  
102 Reaction step  
103 Firing  
104 Wood  
30 104a Heat carrier medium  
105 Mixture
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	106	Pyrolysis gas
	107	Gas product
	108	Lost heat
	109	Formation heat
5	110	Lost heat
	111	Heat feed reaction step
	111a	Heat feed pyrolysis step
	112	Superheated steam
	113	Air
10	114	Excess heat
	115	Heat loss
	116	Waste gas
	117	Water
	118	Mixture
15	401	Material used
	402	Sluice
	403	Shaft kiln
	403a	Line
	404	Feeding
20	405	Grate
	406	Booster
	407	Firing
	408	Worm
	409	Conveyor
25	410	Sluice
	411	Cooling
	412	Sieve
	413	Fine material
	414	Heat carrier medium
30	415	Air
	416	Steam

10	426	Pyrolysis coke
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